The structure of intercalated water in superconducting $Na_{0.35}CoO_2 \cdot 1.37D_2O$: Implications for the superconducting phase diagram

D. N. Argyriou,[1,*] C. J. Milne,[1] N. Aliouane,[1] P.G. Radaelli,[2] L.C. Chapon,[2]
A. Chemseddine,[1] J. Veira,[1] S. Cox,[3] N. D. Mathur,[3] and P. A. Midgley[3]

[1] Hahn-Meitner-Institut, Glienicker Str. 100, Berlin D-14109, Germany
[2] ISIS Facility, Rutherford Appleton Laboratory-CCLRC,
Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom
[3] Department of Materials Science and Metallurgy,
University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, U.K.
(Dated: February 2, 2008)

We have used electron and neutron powder diffraction to elucidate the structural properties of superconducting $Na_xCoO_2 \cdot yD_2O$. Our measurements show that our superconducting sample exhbits a number of supercells ranging from $\frac{1}{3}a^*$ to $\frac{1}{15}a^*$, but the most predominant one, observed also in the neutron data, is a double hexagonal cell with dimensions $2a \times 2a \times c$. Rietveld analysis reveals that D_2O is inserted between CoO_2 sheets as to form a layered network of NaO_6 triangular prisms. Our model removes the need to invoke a 5K superconducting point compound and suggests that a solid solution of Na is possible within a constant amount of water y.

The tuning of Na content in the alkali layered cobaltate Na_xCoO_2 results in remarkable changes in its physical behavior, ranging from magneto-thermoelectricity at $x=0.75$[1] to charge ordering at $x=0.5$[2, 3] and 5K superconductivity at $x=0.3$ after intercalation of H_2O.[4] This interesting combination of physical phenomena occurs within a structural motif reminiscent of geometrically frustrated systems. Here, CoO_2 sheets are constructed by edge sharing CoO_6 octahedra, forming a quasi-2D triangular net. The exact mechanism of superconductivity within this triangular motif is currently the topic of extensive scientific inquiry, as it holds the possibility of realizing Anderson's Resonating Valence Bond model.[5]

Water insertion increases the separation between CoO_2 sheets and band structure calculations suggest that this effectively minimizes the electronic inter-planar coupling.[6, 7]This dimensional cross-over effect is corroborated by measurements showing that T_C increases with the separation between CoO_2 sheets.[8, 9] However, the same measurements also show that T_C does not vary significantly with electronic doping x. This contradicts a proposed analogy between this alkali hydrate and the high-T_C cuprates [10], whereby optimal T_C would occur within a narrow range of electronic doping.

The resolution of this controversy may lie in the details of the crystal structure of this alkali hydrate. Two mutually incompatible structural models of water-intercalated of $Na_xCoO_2 \cdot yH_2O$, have been proposed to date.[11, 12] The model proposed by Lynn et al. asserts that the intercalated water assumes a structure similar to ice[11] between the CoO_2 sheets, whereas the one by Jorgensen et al. suggests a coordination and crystal chemical linkage between Na and H_2O similar that found in many alkali hydrate systems.[12] Both structural models imply that Na concentration x and the amount of intercalated water y are intimately related. But Jorgensen's model also implies that optimal T_C corresponds to a line compound

exhibiting full Na and D_2O ordering with a Na/H_2O ratio $\sim 1/4$.[12]. Both models are based on the parent structure and unit cell, and rely heavily on chemical constraints to interpret the multiple symmetry-equivalent water sites in that cell. In spite of their complexity, these models do not reproduce some important aspects of the data. In particular, an intense Bragg peak at (2.8Å), and a broad distribution of intensity around ($\sim$2.6Å) are not accounted for, although Jorgensen et al. speculate that both features may result from a larger periodicity.

To unravel the complexity of its crystal structure and gain insight into parameters that are critical in establishing a superconducting phase diagram, we clearly need to establish the true translational symmetry of $Na_xCoO_2 \cdot yH_2O$. To this end, we have performed electron diffraction (ED) and neutron powder diffraction (NPD) measurements, the latter employing isotopic H-D substitutions. Both sets of data clearly establish that the dominant ordering mode is a doubling of the hexagonal unit cell along both a and b. Our analysis shows that Na-atoms coordinate with D_2O to form an ordered network of NaO_6 triangular prisms. This model can account well for the intense Bragg reflection in the neutron data at $\sim$2.8Å. ED also shows a number of different superstructures, suggesting significant Na-inhomogeneities. These additional ordering modes are most likely the origin the of a broad distribution of scattered intensity at $\sim$2.6 Å, a common feature of all the neutron data published thus far. Our double-cell model is able to accommodate a variable amount of Na within the same water framework, strongly suggesting that $Na_xCoO_2 \cdot yH_2O$ is not a line compound. Our evidence of more than one Na/water ordering mode within a presumably coherent CoO_2 network should open a serious debate about the true nature of the superconducting phase.

Description of the synthesis and characterization of these samples is found elsewhere.[8] In this work two sam-

ples were investigated with x=0.35, which exhibited a superconducting transitions at 4.5K and 2.8K.[8] ED patterns of these samples were taken using a Philips CM30 transmission electron microscope operated at 300kV with the sample cooled to approximately 90K using a Gatan double tilt liquid nitrogen stage. NPD data were measured from these polycrystalline samples at 2K using the high resolution powder diffractometer E9 (λ=1.7973Å), located at the Berlin Neutron Scattering Center, at the Hahn-Meitner-Institut. Additional data were collected on samples of varying x on the GEM diffractometer at ISIS which were critical in developing the present model, and will be presented elsewhere. To located the O-atoms of the water molecules, the sample with T_C=2.8K that was originally hydrated with D_2O, was exposed to a $(H_2O)_{0.641}$ $(D_2O)_{0.359}$ moisture mixture at a temperature of 26°C for 3 days. This isotopic H/D ratio gives a zero mean coherent neutron scattering length for protons ($\bar{b}_H$=-0.374, $\bar{b}_D$=0.667), so in principle for this sample the contribution of protons to the entire diffraction pattern can be ignored.

Our ED measurements show that the *average* symmetry of the superconducting compound remains hexagonal everywhere. In the majority of grains, super-lattice reflections indicate a cell doubling giving an average unit cell of $2a \times 2a \times c$ (see fig. 1a) where a and c are the lattice constants of the parent $P6_3/mmc$ hexagonal cell. Examination of the NPD data shows the strong reflection observed at 37°(2.8Å) can be assigned to the $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, 1)$ Bragg peaks, as shown in fig. 1c. We can construct a chemically sensible double-cell structural model that fits the 2.8Å peak, providing the strongest indication that this and the ED superlattice reflections have the same origin. Further investigation of the ED data reveals an even more complex superstructure in some areas of the sample as seen in fig. 1b. Satellite reflections, decorating the parent hexagonal lattice reflections, are arranged in hexagonal nets with q-vectors whose magnitude has been seen to vary from $1/15\mathbf{a}^*$ to $1/3\mathbf{a}^*$, but whose direction is always parallel or nearly parallel to $<110>^*$. The example shown in fig 1b corresponds to a supercell translation vector of $3a + 3\frac{2}{3}b$, requiring a *discommensuration* to allow registry between the supercells, equivalent to the Na1-Na2 interatomic vector (see below). In all such patterns mirror symmetry perpendicular to the basal planes is broken as seen by the gross asymmetry in the intensities of satellite reflections of type $\mathbf{g} \pm \mathbf{q}$. However, the 6-fold symmetry appears to be conserved throughout. The detailed superstructure of these modulated phases will be discussed further in a forthcoming publication.

These more complex super-structures seen in the ED measurements are not clearly observed in our NPD data Indeed, an examination of the NPD data does not show the presence of any additional super-lattice reflections above 37° suggesting that disorder (which we model as a
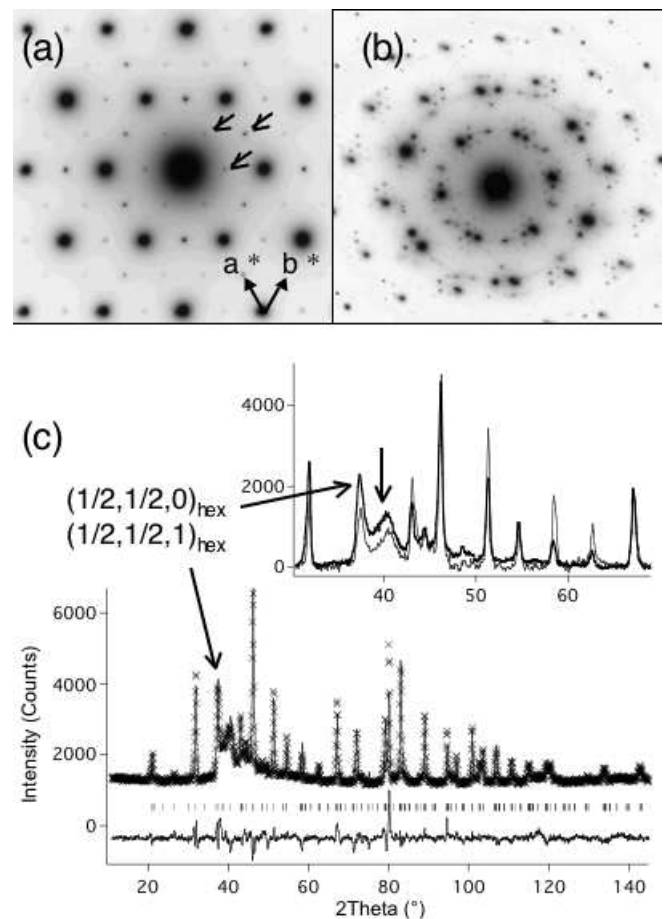

FIG. 1: (a-b) ED patterns from $Na_{0.35}CoO_2.yD_2O$. The arrows in (a) indicate the cell doubling reflections. (c) Neutron powder diffraction data measured at 2K from $Na_{0.35}CoO_2 \cdot yD_2O$. The difference between the observations and the model are plotted under the diffraction pattern, while the expected location of reflection are shown as vertical lines in between. To account for the broad scattering at centered at 40° (indicated by arrow in inset) the background was interpolated manually for the entire pattern. The inset in (c) depicts a portion of the neutron diffractogram from the $Na_{0.35}CoO_2 \cdot yD_2O$ (heavy line) and $Na_{0.35}CoO_2 \cdot y(H_{0.641}D_{0.359})_2O$ (light line). The background arising from the incoherent neutron scattering from H-atoms has been subtracted.

large effective Debye-Waller factor for water) is substantially attenuating their intensity (superstructure reflections in ED are enhanced due to dynamical diffraction). Comparison of the diffractograms from our deuterated and isotopically mixed HD samples show appreciable differences as illustrated in the inset of fig. 1c. While some reflections show no significant change in their intensity with the isotopic substitution (for example $2\theta \sim 31$ and 37°), others do. That the intensity of the super-lattice reflections at 37° as well as the broad feature at 40° is changed, indicates that their structure factor has an appreciable contribution from protons. The origin of the

TABLE I: Structural parameters determined from Rietveld analysis of our NPD data measured from our deuterated $x = 0.35$ sample at 2K. The refined lattice constants were a =5.63477(21)Å and c =19.5456(13)Å (space group P6$_3$/m). The weighted profile R-factor for this refinement is wRp=6.22%. The occupancies of the Na sites were constrained so that $f(Na1) + f(Na2) = 0.35$. The deuterons labeled D31 and D32 are coordinated to O3, and similarly for O4,D41,D42. The refined total amount of D$_2$O was computed to be y=1.37(1). In the Rietveld analysis D$_2$O was inserted as a rigid body, with a D-O bond-length constrained to 0.99 Å and the D-O-D torsion angle set to 108°. U_{iso}(Co,O,Na)=0.0005(2)Å^2 and U_{iso}(D$_2$O)=0.035(4)Å^2. Selected bondlengths (in Å) are given at the bottom of the table.

Atom	x	y	z	f
Co1	0	0	0	1.0
Co2	$\frac{1}{2}$	0	0	1.0
O1	$\frac{1}{3}$	$\frac{2}{3}$	-0.0463(5)	1.0
O2	0.1733(13)	0.3329(15)	0.04756(22)	1.0
Na1	0	0	$\frac{1}{4}$	0.84(4)
Na2	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.56(4)
O3	0.3311(15)	0.3039(19)	0.1722(4)	0.561(5)
D31	0.2226(18)	0.1022(19)	0.1774(7)	= f(O3)
D32	0.2717(27)	0.3539(31)	0.1296(5)	= f(O3)
O4	0.5714(21)	0.1036(26)	0.1849(6)	0.354(7)
D41	0.523(4)	-0.0911(28)	0.1823(12)	= f(O4)
D42	0.6060(26)	0.178(5)	0.1378(8)	= f(O4)

Co1-O2 1.872(7)	Co2-O1 1.861(5)	Co2-O2 1.846(6)	
Co2-O2 1.904 (8)	Na1-O3 2.352(8)	Na1-O4 3.030(4)	
Na2-O3 2.538(10)	Na2-O4 2.484(12)	D32-O2 1.680(11)	
D42-O1 1.945(16)			

broad diffuse feature at 40° (2.6Å) is controversial as it has been described either as an impurity phase[11] or a broad Bragg reflection[12]. We argue below that it may arise from a superposition of Bragg peaks from the additional ordering modes and from short-range order.

To construct a structural model of the Na$_x$CoO$_2 \cdot y$D$_2$O superconductor we analyzed the NPD data using a double hexagonal unit cell ($2a \times 2a \times c$). The space group was identified as P6$_3$/m using symmetry analysis of the parent P6$_3$/mmc space group and taking into consideration the ED observations. The solution of the crystal structure was achieved by first analyzing the isotopically exchanged H-D sample to located the positions of the O-atoms of the water molecules, and then the deuterated sample to located the positions of the protons. This approach produced a good agreement between our model and the NPD data, including the intensity of the reflections at 37°as shown in fig. 1c. Structural parameters and occupancies determined from the Rietveld analysis of the deuterated sample are given, in table I.

The main structural features of our model of superconducting Na$_x$CoO$_2 \cdot y$D$_2$O are shown in figures 2 and 3. The structure of CoO$_2$ sheets does not differ substantially
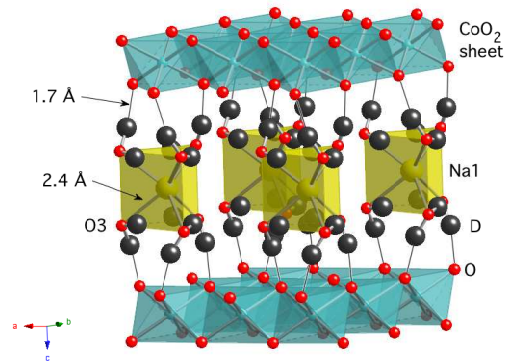

FIG. 2: (Color) A three dimensional representation of the structure of Na$_x$CoO$_2 \cdot y$D$_2$O obtained from our Rietveld analysis. For simplicity we show only half the unit cell along the c-axis and only the Na1 site with the D$_2$O molecule centered at O3. The Na-O3 and D-O(-Co) bond-lengths are shown.

from the one proposed by Takada.[4]. To simplify the discussion of the Na and D$_2$O environment, we first consider an ideal structure of composition $x=\frac{1}{4}$ and y=1.5 consisting of a fully occupied Na1 site surrounded by 6D$_2$O molecules in a triangular prism geometry (see fig. 3a). Each NaO$_6$ prism consists of a Na-atom in the center of the prism and O-atoms at each corner above and below the Na with Na-O bond-lengths of 2.4Å (fig. 2). For this composition, NaO$_6$ prisms would be uncoupled from each other. This is a very typical coordination for Na in Na-hydrate systems.[13] In such materials Na atoms are surrounded by H$_2$O forming *hydration shells*, with the O-atom bonded to the alkali metal with a typical bond length of 2.4Å, while the protons are pointing away from it.[13] The most common Na-H$_2$O coordination is 6, close to the value we find here. The doubling of a and b originates from this ordered arrangement of Na and its hydration shell (see fig. 3). In fact, our NPD analysis has identified two Na sites centered at Na1 $(0,0,\frac{1}{4})$ and Na2 $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$. It is easy to see that additional Na (up to $x=\frac{1}{2}$) with the *same* coordination number can be accommodated into the ideal structure by the progressive filling of the Na2 sites, without a substantial rearrangement of the water molecules. We find that the Na1 site is almost fully occupied with fractional occupancy $f \sim 0.88(4)$, while the second Na2 site is significantly less populated with $f \sim 0.56(4)$. The coordination of O-atoms around the Na2 site is naturally the same as in the Na1, such that NaO$_6$ prisms can be centered at either Na site. The total amount of D$_2$O determined from our Rietveld refinements is y =1.37(1), in good agreement with other reports.[4, 11, 12, 14] Finally our analysis shows that at least one of the protons of the D$_2$O molecule tend to point toward the CoO$_2$ sheets forming a hydrogen bond (D-O=1.7 Å) with an O-atom in that layer (fig. 2). The structural model we employed in our best fits is slightly more complex than the one we just described, in that

it includes a small amount of additional water centered around the O4 position (see table). This position, equivalent to the O3 position in the parent unit cell, may represent contributions of the four possible coherent domains of the double hexagonal cell. More likely, however, this site helps modeling the large amount of disorder in the structure (see below).

The main implication of our model, and the most relevant for the physics of this compound, is that $Na_xCoO_2 \cdot yH_2O$ has the *potential* of being a homogeneous solid solution in a wide range of Na concentrations, rather than a point compound as suggested by Jorgensen *et al.* [12]. A second important implication is that changes of Na content can, within limits, be accommodated at constant water content, as each O-atom of the D_2O molecule locally will be coordinated two Na-atoms. In reality, a series of more or less stable ordered arrangements of Na2 occupied and vacant sites will occur for specific Na concentrations, although not all of them will be kinetically accessible. The complex synthesis route of this material (de-intercalation of Na and intercalation of water) helps to explain why more than one superstructure type is observed in the same sample. The inhomogeneous distribution of Na that is expected from de-intercalation produces a *disordered background* on which intercalated H_2O must arrange. The intercalation of water would yield some re-organization of the Na-atoms at the local scale, but energetically a global re-arrangement is too costly (unless an anneal is possible). As water is inserted into the lattice, local ordering of Na atoms occurs that resembles as much as possible the structure we describe. Fluctuations in the Na concentration are accommodated locally into the Na2-site, occasionally reaching an appropriate value for the formation of a long-period superstructure. This model would account for the predominant doubling mode and the many other diverse superstructures observed by ED. We note that our model does fold onto the structural models proposed thus far.[11, 12] For example the Na1 site of the model by Lynn *et al.* maps onto the Na1 site of our model and similarly for the model of Jorgensen *et al.* and the Na2 site.

The presence of these inhomogeneities should lead one to reconsider carefully the true nature of the superconducting phase. For example the predominant $2a \times 2a \times c$ ordering may represent the 5K superconducting point phase while other supercells may also be superconducting with a lower T_C. This scenario is consistent with the almost constant variation of T_C that has been observed as function x;[8] NPD data over a range of x that we have measured ($0.28 < x < 0.37$) display the $(\frac{1}{2}, \frac{1}{2}, 0)$-$(\frac{1}{2}, \frac{1}{2}, 1)$ super-lattice reflection pair, indicating that the predominate of this ordering is quite stable over this x-range. Other scenarios are possible, such as those in which a minority phase would be superconducting, and would partially shield the majority non-superconducting phase, but this is unlikely as superconducting fractions are high,
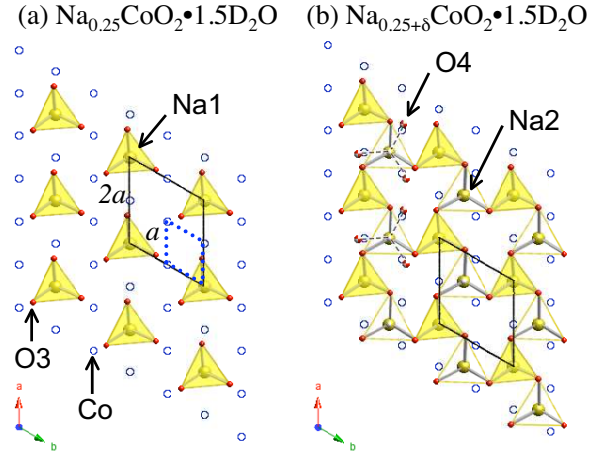
(a) $Na_{0.25}CoO_2 \bullet 1.5D_2O$ (b) $Na_{0.25+\delta}CoO_2 \bullet 1.5D_2O$

FIG. 3: (Color) Projections of the Na-D_2O layer down the $c-$axis. The NaO_6 triangular prisms centered on Na are highlighted. The $2a \times 2a \times c$ unit cell is shown in solid lines and the $a \times a \times c$ cell as dashed lines. The doubling of the unit cell is evident from the position of the Na sites. D-atoms are omitted for clarity. (a) The idealized $x = \frac{1}{4}$ structure. (b) A model for the $x = \frac{1}{2}$ structure with the Na2 site filled. The coordination to the O4 site is shown.

indicating that a majority phase is a superconductor.

In summary, our neutron and electron diffraction data have unraveled a new aspect of the structure of $Na_xCoO_2 \cdot yD_2O$, shedding light into its material and physical properties. The formation of a NaO_6 triangular prism network can sustain a large range of x, without the necessity to vary the water content, or the separation between CoO_2 sheets. We argue on the basis of the structure that the amount of intercalated water essentially defines the separation between CoO_2 sheets and thus T_C. A variety of sodium dopings, some of which leads to additional ordering can be accommodated in the structure and should have little influence on separation of CoO_2 sheets as Na can be distributed over two sites that coordinate to one water molecule, while maintain an average coordination close to the ideal Na-$6D_2O$.

* Email of corresponding author: argyriou@hmi.de
[1] Y. Wang, et al., Nature **65**, 423 (425).
[2] Q. Q. Huang, et al.,cond-mat/0402255 (2004).
[3] I. Mukhamedshin, et al.,cond-mat/0402074 (2004).
[4] K. Takada, et al., Nature **422**, 53 (2003).
[5] G. Baskaran, Phys. Rev. Lett. **91**, 097003 (2003).
[6] M. D. Johannes and et al.,cond-mat/0401646 (2004).
[7] C. A. Marianetti, et al.,cond-mat/0312514 (2003).
[8] C. J. Milne, and et al.,cond-mat/0401273 (2004).
[9] D. P. Chen, et al.,C. T. Lin, cond-mat/0401636 (2004).
[10] R. Schaak, et al.,Nature **424**, 527 (2003).
[11] J. W. Lynn, et al., Phys Rev B **68**, 214516 (2003).
[12] J. D. Jorgensen, et al., Phys. Rev B **68**, 214517 (2003).
[13] S. Obst and H. Bradaczek, J. of Phys. Chem. **100**, 15677 (1996).
[14] M. Foo, et al., Solid State Comm. **127** (2003).